Chapter 21

The Activity and Selectivity Properties of Supported Metal Oxide Catalysts During Oxidation Reactions

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Structure-reactivity studies involving model supported metal oxide catalysts reveal that the efficiency of a particular selective oxidation reaction depends on the specific supported metal oxide species, the coverage of the surface metal oxide species, the oxide support, and the presence of secondary metal oxide additives. *In situ* Raman spectroscopy, activity, and selectivity of the partial oxidation of methanol, alkanes, and the selective catalytic reduction of NO with ammonia are discussed with respect to the above factors for supported metal oxide catalysts.

Supported metal oxide catalysts are extensively employed in the petrochemical and pollution control industries as oxidation catalysts. For example, titania supported vanadia catalysts are used for the selective oxidation of o-xylene to phthalic anhydride, ammoxidation of aromatic methyl groups and the selective catalytic reduction (SCR) of NO_x with ammonia. The active redox components (V, Mo, Cr or Re) of supported metal oxide catalysts are present as two-dimensional metal oxide overlayers on the high surface area oxide supports (e.g., titania, alumina, silica, niobia, zirconia, etc.). Such supported metal oxide catalysts are also ideal model systems to study the fundamental aspects of selective oxidation reactions because the active surface redox sites can be molecularly characterized with *in situ* Raman, IR, solid state NMR, DRS and EXAFS/XANES. Furthermore, the environment around the active redox sites can also be varied by changing the surface metal oxide coverage, changing the specific oxide support or by the addition of secondary metal oxide additives (e.g., oxides of W, Nb, P, etc.) to the two-dimensional overlayer. In the present investigation, Raman

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spectroscopy was primarily employed to obtain information about the molecular structures present in the two-dimensional overlayers and methanol oxidation was primarily used to chemically probe the surface redox as well as acid sites. Combination of this information with catalytic data for the selective oxidation of alkanes and the selective reduction of NO with ammonia has provided new insights into the origin of the activity and selectivity properties of supported metal oxide catalysts during oxidation reactions.

Molecular structures of the surface metal oxide species

The molecular structures of the oxidized and dehydrated surface metal oxide species have been extensively investigated with *in situ* Raman spectroscopy as well as other spectroscopies and have been reported elsewhere *(1-8)*. Surface rhenium oxide species are present as isolated, tetrahedrally coordinated ReO_4 species *(2)*. In contrast, surface chromium oxide species are primarily present as polymerized surface CrO_4 species *(3)*. Surface vanadium oxide species are also tetrahedrally coordinated and favor isolated surface species at low coverages and polymerized surface species at high coverages *(4-7)*. Surface molybdenum oxide species favor isolated, tetrahedral coordination at low coverages and polymerized, octahedral species at high coverages *(8)*. An exception to the above trends is when silica is employed as a support since the surface metal oxide species are usually not polymerized on the silica surface due to the low surface metal oxide densities achievable on this somewhat unreactive substrate. All the surface metal oxide species form highly distorted structures containing terminal M=O bonds and bridging M-O-M' bonds where M' represents the same or another surface metal oxide species or the oxide support *(1-8)*.

The influence of different reaction environments upon the state of the surface metal oxide species during oxidation reactions have recently been investigated with *in situ* Raman spectroscopy. During methanol oxidation, a significant portion of the surface metal oxide species are reduced and the fraction reduced is not a function of the specific oxide support *(9,10)*. In contrast, the fraction of the surface vanadia species reduced during alkane (methane and butane) oxidation is a function of the specific oxide support *(11,12)*. During alkane oxidation the surface vanadia species are not reduced for V_2O_5/SiO_2, but are partially reduced for V_2O_5/TiO_2, V_2O_5/ZrO_2, V_2O_5/Nb_2O_5, V_2O_5/CeO_2 and V_2O_5/SnO_2. The selective catalytic reduction of NO with ammonia at elevated temperatures appears to cause only slight or no reduction of the surface vanadia species on titania because of the very low concentrations of ammonia and the high concentrations of oxygen typically employed for this commercial reaction *(13)*. Thus, under oxidation reaction conditions, both fully oxidized and partially reduced surface metal oxide species are present and the extent of reduction appears to depend on the reducing power (defined as the ability to reduce the surface metal oxide active site) of the specific reactant molecule (methanol > butane ~ methane), the concentration of the reactant molecules (NO reduction with ammonia) and the specific oxide support.

The molecular structures of the secondary surface metal oxide additives (e.g., oxides of W, Nb and P) have also been determined *(14)*. The surface tungsten oxide and niobium oxide species are primarily present as highly distorted, octahedrally coordinated species and the surface phosphorous oxide species possesses tetrahedral coordination. These surface metal oxide additives are generally non-reducible under most reaction conditions, but may become partially reduced at elevated temperatures on certain oxide supports.

Catalytic activity

The reactivity properties of supported metal oxide catalysts during methanol oxidation have been recently reviewed and will only be briefly discussed here *(1)*. The two-dimensional nature of the active surface metal oxide species allows the reaction rates to be expressed as turnover frequencies (TOF), which is the number of methanol molecules converted per active redox atom per second. The methanol oxidation TOF was found to essentially be independent of the surface coverage of the surface redox sites which suggests that this oxidation reaction requires only one surface redox site to proceed. A similar conclusion was also reached for methanol oxidation over model Keggin metal oxide catalysts *(15,16)*. The methanol oxidation TOF was also not influenced by the presence of other non-reducible surface metal oxide species in the two-dimensional overlayer (e.g., oxides of W, Nb, Si and S) and is consistent with the conclusion that only one redox site is required for this reaction *(14)*. However, the specific oxide support had a pronounced effect on this reaction and the TOF varied by several orders of magnitude (Ce > Ti ~ Zr > Nb > Al > Si) *(1)* as shown in Table I. It has been proposed that the origin of this dramatic support effect is due to the involvement of the bridging M-O-support bonds in the rate determining step and the observed trend correlates with the basicity or electronegativity of the oxygens associated with the oxide support. Recent theoretical calculations are in agreement with this model *(17-19)*. The specific surface redox site also had an effect on the TOF and the surface V and Re oxides were approximately an order of magnitude more active than the surface Mo and Cr oxides. Thus, for oxidation reactions requiring only one surface redox site the TOF is only influenced by the specific oxide support and the specific surface redox site.

Table I. The TOF of methanol oxidation over supported vanadia catalysts as a function of the oxide support

1% V_2O_5 on oxide support	*TOF (s^{-1})*
CeO_2	~$1x10^1$
TiO_2	$2.0x10^0$
ZrO_2	$1.6x10^0$
Nb_2O_5	$8.0x10^{-1}$
Al_2O_3	$3.6x10^{-2}$
SiO_2	$3.9x10^{-3}$

The TOF for the oxidation of alkanes over supported vanadium oxide catalysts behaved very similarly to the TOF for methanol oxidation *(11,12,20)*: the TOF was independent of surface vanadia coverage and secondary non-reducible surface metal oxide additives, but significantly varied with the specific oxide support. This suggests that activation of alkanes requires only one surface redox site.

In contrast to the above oxidation reactions, the SCR of NO with ammonia exhibits a TOF that is a strong function of surface coverage and the presence of non-reducible surface metal oxide additives *(21)*. This TOF pattern suggests that the SCR reaction requires two surface sites to proceed: a surface redox site and an adjacent surface non-reducible metal oxide site *(21-23)*. The SCR TOF also varied with the specific oxide support and the specific surface metal oxide redox site since these parameters control the redox properties of the surface metal oxide species *(21,24,25)*.

Catalytic selectivity

The selectivity properties of supported metal oxide catalysts during methanol oxidation to formaldehyde depend on the specific oxide support, the specific surface metal oxide redox site and the surface coverage. Comparision of the Lewis acidity data from pyridine adsorption experiments (strength of Lewis sites Al > Nb > Ti ~ Zr and no acid sites on Si *(26)*) and the methanol oxidation activity and selectivity data of the oxide supports *(27)* suggests that the surface Lewis acid sites present on the oxide supports are responsible for the non-selective formation of dimethyl ether and the surface redox sites present on zirconia are responsible for the formation of methylformate as shown in Table II *(27)*. In all cases, the contribution of the support towards these side reactions is minimized as the surface coverage of the surface metal oxide redox sites is increased towards monolayer coverage as shown in Table III for supported vanadium oxide catalysts *(9,27)*. The highest formaldehyde selectivities were found for the titania supported metal oxide catalysts because titania possessed the weakest Lewis acid sites and did not possess significant surface redox sites. The selectivity towards formaldehyde was strongly dependent on the specific surface metal oxide redox site for titania supported catalysts (V (95-99%) > Mo (75-82%) > Cr (70%) ~Re (70%)) where the primary side reaction was the formation of methylformate *(28,29)*. The formation of methylformate correlated with the intrinsic acidic properties of these metal oxides *(30,31)*. The addition of non-reducible surface metal oxide species (W, Nb, Si and S) to the two-dimensional surface metal oxide overlayer did not influence the selectivity towards formaldehyde as shown in Table IV *(14,21)*. Thus, the most selective supported metal oxide catalyst for methanol oxidation to formaldehyde consisted of the surface metal oxide redox site that possessed the weakest acidic character, vanadium oxide, and the oxide support that possessed both weak surface acid and redox sites, titania.

The selectivity pattern for alkane oxidation over the supported vanadia catalysts depended on the specific alkane oxidation reaction. For methane oxidation over silica supported vanadia catalysts, the selectivity was a function of methane conversion since formaldehyde was further oxidized to carbon monoxide. At the high temperatures required to conduct this oxidation reaction, the fate of gas-phase methyl radicals may also be an important parameter on the reaction selectivity *(11)*. The selective oxidation of methane over supported vanadia catalysts was also very sensitive to the specific oxide support since formaldehyde could be further oxidized to carbon dioxide depending on the reducibility of the oxide support (Sn > Ti > Si) *(11)*. The selectivity of propane oxidation to propylene was not a function of the surface vanadia coverage or propane conversion *(20)*. The selectivity of butane oxidation to maleic anhydride/acid was not a strong function of the specific oxide support, but was influenced by the surface coverage *(12)*. The selectivity to maleic increased with surface coverage which reflects the higher efficiency of this reaction path when two adjacent surface vanadia species are present. The introduction of surface Lewis acid sites, surface niobia and tungsten oxide species, slightly increased the maleic selectivity. Thus, the selectivity of alkane oxidation reactions involving only the abstraction of hydrogen is less sensitive to their immediate environments than alkane oxidation reactions involving the insertion of oxygen.

Table II. The activities and selectivities of the oxide supports during methanol oxidation

Oxide Support	*Activity (mol CH_3OH conv./ g.hr)*	*Selectivity (%)* *FA*	*MF*	*DMM*	*DME*	*CO_x*
Al_2O_3	$3.7x10^0$	--	--	--	100	--
Nb_2O_5	$1.0x10^{-2}$	--	--	--	100	--
TiO_2	$2.0x10^{-3}$	--	--	--	91	9
ZrO_2	$2.0x10^{-2}$	--	86	--	Tr	14
SiO_2	$2.6x10^{-4}$	--	--	--	15	85

Table III. The methanol oxidation selectivities as a function of surface coverage for V_2O_5/Al_2O_3 catalysts

Catalyst	*Selectivity(%)* *FA*	*MF*	*DMM*	*DME*	*CO_x*
Al_2O_3	--	--	--	100	--
1% V_2O_5/Al_2O_3	<1	--	--	99	--
3% V_2O_5/Al_2O_3	2	--	--	97	Tr
10% V_2O_5/Al_2O_3	16	--	Tr	84	--
15% V_2O_5/Al_2O_3	22	--	1	77	--
20% V_2O_5/Al_2O_3	46	--	3	50	Tr

The selective formation of nitrogen during the SCR of NO with ammonia is dependent on the specific oxide support, the specific surface metal oxide redox site, surface coverage and the presence of non-reducible surface metal oxide species *(21,25)*. The selectivity pattern follows the same trend as observed for methanol oxidation to formaldehyde (V > Cr > Re) and suggests that it is related to the intrinsic properties of the specific surface metal oxide species. However, the selectivity decreases with increasing coverage due to oxidation of ammonia by too many adjacent surface redox sites at elevated temperatures. The selectivity may also be decreased by the addition of non-reducible secondary surface metal oxide additives that may become active for the oxidation of ammonia at elevated temperatures on a reducible oxide support such as titania. The selectivity is also dependent on the specific oxide support (Ti > Al > Si). Thus, the selectivity of the SCR reaction is sensitive to all variations since it is a reaction that requires two adjacent sites.

Table IV. Effect of additives on the selectivity of methanol oxidation

Catalyst	*Selectivity(%)*				
	FA	*MF*	*DMM*	*DME*	CO_x
1% V_2O_5/TiO_2	99+	--	--	Tr	--
6% Nb_2O_5/ 1% V_2O_5/TiO_2	97	--	2	1	--
7% WO_3/ 1% V_2O_5/TiO_2	93	--	5	2	--
3% SiO_2/ 1% V_2O_5/TiO_2	96	--	3	Tr	Tr

Conclusions

Under oxidation reaction conditions, the surface metal oxide species may exhibit both fully oxidized and partially reduced surface redox sites. The extent of reduction depends on the reducing power of the reactant (methanol >> butane ~ methane) as well as the concentration of the reducing agent (e.g., SCR of NO with ammonia). The specific oxide support may also influence the extent of reduction of the surface metal oxide species for certain reactions (e.g., during alkane oxidation Sn > Ti ~ Zr > Al > Si).

The TOF of a specific oxidation reaction depends on the specific oxide support and the specific surface redox site. In general, the more reducible oxide supports result in more active ligands for the surface metal oxide species (Sn > Ce > Zr ~ Ti > Nb > Al > Si). For oxidation reactions that require one surface redox site (e.g., methanol, methane, propane and butane), the TOF is generally not influenced by surface metal oxide coverage and the presence of non-reducible secondary surface metal oxide additives. For oxidation reactions that require more than one surface site, two surface redox sites or a surface redox site and an adjacent surface acid site (e.g., SCR of NO with ammonia), the TOF is influenced by surface metal oxide coverage and the presence of secondary metal oxide species.

The selectivity properties of a specific oxidation reaction may depend on the nature of the oxide support, the surface metal oxide species, the surface coverage of the surface metal oxide species and the presence of secondary surface metal oxide additives. Surface vanadium oxide species appear to be the most selective surface redox sites during oxidation reactions. For methanol oxidation to formaldehyde, the most selective supported metal oxide catalyst consists of the surface metal oxide redox site that possesses the weakest acidic character and the oxide support that possesses both weak surface acid and redox sites: V_2O_5/TiO_2. These same properties are also responsible for making the V_2O_5/TiO_2 catalyst system one of the most selective catalysts for the SCR of NO with ammonia and oxidation of butane to maleic anhydride. For methane oxidation to formaldehyde, which generally occurs at much higher temperatures than the other oxidation reactions, a relatively inert oxide support, essentially possessing no surface acid or redox sites, that will minimize the decomposition of gas-phase methyl radicals and the further oxidation of formaldehyde is required and the most effective catalyst is V_2O_5/SiO_2. Surface coverage of the surface metal oxide species is generally an important parameter in modulating the selectivity since it can suppress side reactions that are associated with the oxide support (e.g., methanol oxidation and methane oxidation) and affect reactions that require two adjacent sites (SCR of NO with ammonia and the selective oxidation of butane to maleic anhydride). Similarly, secondary surface metal oxide additives can also modulate the reaction selectivity by influencing side reactions or enhancing the desired reaction (especially if the reaction requires two adjacent surface sites). Thus, each type of oxidation reaction has specific selectivity requirements which depend on the functional groups to be oxidized.

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